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Palladium-catalyzed carbonylative synthesis of carboxylic acid anhydrides from Alkenes

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Curriculum Vitae

Ashok Ramakrishnan was born on 11th September, 1991, in Kerala, India. After high school, he pursued Bachelors in Pharmacy (B.Pharm) at Mumbai University from 2009 to 2013 and graduated with distinction. He was awarded a scholarship from the Sir Ratan Tata Trust, which he received from 2011 to 2013.

Subsequently, he was admitted in one of the top institutes for pharmacy education in India – National Institute for Pharmacy Education and Research (NIPER), Mohali, where he pursued a Master's in Medicinal Chemistry (M.S. Pharm). During his master's program, Ashok conducted his thesis research under the guidance of Prof. dr. P.V. Bharatam. His thesis, entitled "Tautomerism in biologically active hydrazone derivatives and exploration of divalent N(I) character", delved into the experimental and computational study of azine-hydrazone tautomerism in amidinohydrazone derivatives. Additionally, he explored the presence of divalent N(I) character in these compounds and synthesized several amidinohydrazone derivatives to test for their anti-leishmanial activity. Ashok earned a scholarship from Bristol-Myers-Squib (BMS) during this period. He published his first research paper, "Azine or hydrazone? The dilemma in amidinohydrazone derivatives," in RSC Advances before graduating with high honors in July 2015.

Following the completion of his master's degree, Ashok ventured into industrial research with a focus on organic synthesis, a field he pursued until the end of 2018. During this period, he also worked in the peptide synthetic division of the biopharma company - Biocon Ltd., currently ranked 8th among Global Biotech Employers for 2022 by Science magazine. In January 2019, he joined the group of Prof. dr. Elisabeth Bouwman for a PhD in 'Homogenous Catalysis' in the department, 'Metals in Catalysis, Biomimetics and Inorganic Materials' (MCBIM), at the Leiden Institute of Chemistry (LIC). He supervised several practical courses for bachelor students during his PhD. Ashok followed a number of courses offered by the Holland Research School of Molecular Chemistry (HRSMC) as well as the Graduate School of Leiden University, including "Scientific Conduct", "Physical Methods in Inorganic Chemistry", "Molecular Modelling", "High Impact Writing" and "Organic Synthesis Summer School 2021". He also attended the course, 'Catalysis An Integrated Approach (CAIA)' offered by Nederlands Instituut voor Onderzoek in de Katalyse (NIOK) and passed the related exam. Further, he attended several conferences (as listed below) wherein the results reported in this thesis were presented:

2022

- Oral presentation at Chemistry As Innovating Science (CHAINS) 2022 by NWO at Veldhoven, The Netherlands
- Attended the International Symposium on Homogenous Catalysis 2022 at Lisbon, Portugal
- Poster presentation at Holland Research School of Molecular Chemistry (HRSMC) Symposium 2021 (held in March '22) at Amsterdam, The Netherlands

2021

- Presented poster at CHAINS 2021 by NWO at Veldhoven, The Netherlands
- Presented poster at the Organic Synthesis Summer School 2021 conducted by HRSMC, The Netherlands

2020

- Presented poster at Netherlands' Catalysis and Chemistry Conference (NCCC) 2020 at Noordwijkerhout, The Netherlands

List of Publications

1. Ramakrishnan, A.; Chourasiya, S. S.; Bharatam, P. V. Azine or Hydrazone? The Dilemma in Amidinohydrazone. *RSC Adv.* **2015**, 5 (69), 55938–55947.
2. Chourasiya, S. S.; Kathuria, D.; Nikam, S. S.; Ramakrishnan, A.; Khullar, S.; Mandal, S. K.; Chakraborti, A. K.; Bharatam, P. V. Azine-Hydrazone Tautomerism of Guanyldihydrazone: Evidence for the Preference Toward the Azine Tautomer. *J. Org. Chem.* **2016**, 81 (17), 7574–7583.
3. Liu, C.; van den Bos, D.; den Hartog, B.; van der Meij, D.; Ramakrishnan, A.; Bonnet, S. Ligand Controls the Activity of Light-Driven Water Oxidation Catalyzed by Nickel(II) Porphyrin Complexes in Neutral Homogeneous Aqueous Solutions. *Angew. Chem. Int. Ed.* **2021**, 60 (24), 13463–13469.
4. Ramakrishnan, A.; Romeijn, S. G.; Bouwman, E. Palladium-Catalyzed Synthesis of Carboxylic Acid Anhydrides from Alkenes. *J. Catal.* **2023**, *in press*, DOI: 10.1016/j.jcat.2023.115192.
5. Ramakrishnan, A.; Bouwman, E. Regioselectivity in Carbonylation of Pentenoic Acid to Synthesize Cyclic Anhydrides, *manuscript submitted*.
6. Ramakrishnan, A.; Bouwman, E. Palladium-Catalyzed Synthesis of Symmetric Carboxylic Acid Anhydrides from Alkenes with *in situ* Generated Carboxylic Acids, *manuscript in preparation*.

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First and foremost, I am immensely grateful to Prof. dr. Elisabeth Bouwman for granting me the opportunity to pursue my PhD in her group. Her unwavering encouragement I received to critically think and question every result, to present results effectively and for allowing scientific flexibility and freedom, is truly beyond measure. The countless work discussions, brainstorming sessions, and spirited scientific debates unquestionably shaped the outcome of this research and helped me complete my thesis. I would like to thank my second promotor, Dr. Dennis Hetterscheid, for his suggestions during group meetings as well as for improving this thesis. I also would like to thank Prof. dr. Sylvestre Bonnet for the scientific suggestions and feedback provided during this research.

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Ashok Ramakrishnan